

CHARACTERIZATION OF THE LTC CATALYST:
PERFORMANCE AGAINST COMMON AIR POLLUTANTS

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SUMMARY

One of the important qualities of the LTC* catalyst is the rapid oxidation of carbon monoxide to carbon dioxide under a wide variety of conditions. The catalytic material is a palladium-copper activated complex which reacts with various contaminant molecules through a continuous oxidation/reduction cycle. The alumina substrate enhances LTC activity with its favorable surface chemistry and very high surface area. About 10 percent surface water is necessary to facilitate the oxidation of CO. This reaction shows a log-log dependence on contact time, suggesting a Langmuir-Hinshelwood mechanism.

In the tube tests, LTC removed 90 to 100 percent of contaminating carbon monoxide in the temperature region of 20° to 400°C, and at ambient over a range of 25 to 65 percent relative humidity. In contrast, NO₂ is chemisorbed by the LTC/alumina material--the amount strongly dependent on temperature increases but independent of humidity.

Performance tests in the Instapure® Air Filtration appliance were done in a sealed room using 300 cfm air flow rate. The CO was 78 percent removed, O₃ 100 percent removed, SO₂ and H₂S 100 percent, NH₃ 58 percent, NO₂ 40 percent, and benzene 8 percent removed. The CO from sidestream tobacco smoke was 34 percent removed by the appliance. Hazardous components of mainstream tobacco smoke were effectively reduced using a small ancillary filter containing LTC.

The LTC catalyst has demonstrated excellent capability to remove an important variety of hazardous pollutant gases which are common factors to poor indoor air quality. The Instapure® Air Filtration System incorporates the LTC catalyst in a 50:50 mixture with activated carbon to effectively remove particulate, odors, and hazardous gases at room temperature and humidities. The ability to remove hazardous gases is unique for the category of portable air filtration equipment. The wide variety of pollutant gases that LTC removes suggests the catalytic technology is adaptable to a considerable range of commercial and industrial applications.

INTRODUCTION

The Environmental Protection Agency has been conducting various studies of indoor air contaminants and their exposure effects.^{1,2,3} These results and others indicate that personal exposure to specific pollutants is often significantly greater than outdoor exposure limits. Tightening up of residences for reasons of energy conservation, greater use of synthetic materials in building and furnishing interiors, tobacco smoking, and increased use of solvents all are major contributors to the deterioration of indoor air quality.

*Low-Temperature Catalyst (LTC).

Most individuals spend up to 90 percent of their time indoors; about 70 percent is in residential and office environments. The various types of pollutants--as particulate, or harmful gases--have been linked to ill health effects. Currently, the most controversial issue is the effect of sidestream tobacco smoke on non-smokers in the same environment.

As reported in an earlier paper,⁴ Teledyne Water Pik has developed a novel room temperature catalyst (LTC) for removal of various gaseous contaminants. In particular, this catalyst oxidizes carbon monoxide to carbon dioxide at very efficient rates. It also has shown good rates of removal for ozone, nitrogen and sulfur oxides, hydrogen sulfide, ammonia, and certain toxic components of cigarette smoke.

LTC CATALYST MATERIAL

In general, the LTC catalyst consists of a solution of copper and palladium salts deposited on a porous alumina substrate. It appears that this substrate material provides a certain enhancement of catalytic activity due to its specific surface chemistry, as well as large surface area for dispersion of the LTC composition. Also a minimum of post-deposition water content, tightly held by the alumina, is necessary to achieve reasonable rates of catalytic efficiency.

Reaction Mechanism

The reaction of LTC with carbon monoxide is analogous to the Wacker commercial process for producing acetaldehyde.⁵ The oxidation-reduction cycle requires exchange of electrons between the copper and palladium metals of the complex; water is both consumed and returned to the catalytic cycle.

A simplified diagram of this reaction is shown in Figure 1. The deposits of metal salts contain activated complexes which create sites for selective chemisorption of oxygen and carbon monoxide. Present theory holds that "islands of atomic oxygen are adsorbed, surrounded by carbon monoxide molecules and that the oxidation reaction occurs at their interface."⁶ The rate of reaction is determined by the catalyst's efficiency.

LTC Activated Complex

Several simple tests imply the formation of a palladium-copper complex, probably stabilized by surrounding anions. This complex is the active species which is responsible for catalytic rates of CO oxidation to CO₂.

A "catalyst" made with only the palladium salt--all else equal--was able to achieve 50 percent CO removal under standard tube test conditions. Likewise, a "catalyst" containing the two copper salts gave only 15 and decaying to 4 percent CO removal. The LTC combination of these three salts consistently removes greater than 85 percent CO.

A series of tests using stepwise additions of the metal salts constituents in various sequences (same final composition) clearly shows the best CO removals occur with the simultaneous deposit of the LTC composition.

SPECIFICATIONS FOR PERFORMANCE TESTS

Tube Test for Catalytic Activity

A one gram sample of LTC catalyst is packed in a glass tube to minimize by-pass and exposed to feed gas flow of known concentration in a single contaminant. Relative humidity in the feed stream may be varied from 10 to 90 percent, while temperature is unregulated ambient. Typical test conditions are 50 parts per million of carbon monoxide and 60 percent relative humidity at a flow rate of 500 cc/minute. The difference in CO concentration between feed gas passed over untreated substrate alumina beads versus over the LTC catalyst measures activity, which can be monitored over time. Equilibrium removal rates are the percentage of pollutant concentration lost after 6 hours. The standard deviation of 8 repetitive test results was a satisfying 2.1.

The actual amount of contaminant removed, of course, depends on physical parameters--the amount of LTC, the size and thickness of the catalyst bed, gas flow rate, length of testing, and initial concentration of contaminant CO. Time of contact with LTC reflects the former variables and is calculated from:

$$\ln (C_0/C_t) = K \cdot t_c \quad (1)$$

Assuming a first-order reaction rate (oxidation of CO to CO₂), C_t is the contaminant concentration at some time t, C₀ is the initial concentration, K is the reaction rate constant, and t_c is contact time. In reality, the reaction rate also varies with the amount of surface coverage of oxygen and carbon monoxide, therefore a first-order reaction scheme is a considerable simplification. The reaction constant is characteristic of catalyst material, independent of test procedures. For example, an LTC catalyst with an equilibrium CO removal rate of 93 percent has a calculated K of about 12 seconds⁻¹.

Room Test of Air Filtration Appliance

The second type of performance test measures contaminant removal in a sealed room, using the LTC catalyst filter in our air filtration appliance. Filters were designed to hold about 230 grams of LTC catalyst in a thin bed with minimal air flow by-pass. This test is conducted in a 1008 cubic foot stainless-steel room with an initially known amount of gaseous contaminant. The rate of decay is subtracted from the performance of the appliance. Air flow through the appliance was 300 cfm for the test duration of 2 hours. The standard deviation of 7 repetitive test results was an excellent 1.4.

TUBE TEST PERFORMANCE

Temperature Dependence

The temperature dependence of LTC performance has been reported previously,⁴ but a brief description is included for completeness. Figure 2 maps results of a series of tests for CO removal of LTC at various temperatures. Between room temperature and about 400°C, CO oxidation ranges between 90 and 100 percent. Below about 65°F, the reaction rate drops off sharply, probably as a result of increased dissipation of the heat of reaction.

In contrast, the physical adsorption of NO₂ decreases as the temperature increases. Near 100 percent adsorption occurs between -50° and 25°C, gradually decreasing to 50 percent at 175°C.

Relative Humidity Dependence

The dependence of LTC activity on relative humidity was also reported previously,⁴ and is illustrated in Figure 3. The CO oxidation is optimum between about 25 to 70 percent relative humidity. Inadequate water present inhibits the reaction at interfaces of adsorbed "island oxygen" and surrounding CO molecules. Too much moisture fills the micropores of the alumina, effectively "drowning" these active metal deposits.

The physical adsorption of NO₂ is unaffected by humidity, presumably because most of the chemisorption is on the surface of the LTC/alumina bead and in the macropores. A common commercial material, Hopcalite, is severely poisoned by water vapor; it is ineffective above 10 percent relative humidity.

Contact Time

One of the physical parameters which strongly affects the LTC rate of CO oxidation is the time that the contaminant is in contact with the catalyst. Table I shows data for contact times of 0.4 to 0.01 second, achieved by varying the gas flow rate (5 to 0.5 Lpm) and/or the bed depth of LTC packed in the tube. All tests were conducted at room temperature and 60 percent relative humidity with 50 parts per million CO.

TABLE I
Effect of contact time on CO oxidation.

Contact Time (Sec.)	Bed Depth (Inches)	% Average CO Removal
0.4	1.0	84
0.2	0.5	52
0.1	0.5	30
0.08	0.4	28
0.05	0.25	14
0.025	0.25	7
0.01	0.25	2

Although Equation 1 postulates a log-linear plot, the data fit a log-log curve--confirmed by regression analysis. The amount of surface coverage of the active LTC sites with CO and oxygen molecules accounts in large part for the discrepancy, as well as the fact that the oxygen-palladium bonds are weakened by the co-adsorption of CO molecules.⁶ Thus, the reaction conforms more closely to the Langmuir-Hinshelwood mechanism rather than a simple first order dependency.⁷

ROOM TEST PERFORMANCE RESULTS

One present application of the LTC catalyst is a portable air filtration appliance for home and office environments. The LTC beads are tightly packed into a thin filter to minimize pressure drop; in the product filters LTC and activated carbon are mixed 50:50. The Instapure® Air Filtration System units used in this series of tests had LTC only (about 230 grams) and an air flow rate of 300 cfm. The contact time is thus approximately 0.02 second, or an order of magnitude less than that in the tube test. All of the following tests were conducted in a 1008 cubic foot sealed room at 40 percent relative humidity and ambient temperature. Initial contaminant concentrations are noted in each test, each of 2 hour duration. Figure 4 summarizes all of the results as adjusted for each species' rate of decay. The Threshold Limit Value--Short Term Exposure Limit (STEL) values are recommendations issued by the American Conference of Governmental Industrial Hygienists (1983).⁸ The STEL values cited are for a 15 minute time-weighted average which should not be exceeded during a work day.

Carbon Monoxide

A filter using 50:50 LTC to activated carbon was tested, using 30 parts per million CO to begin. The STEL limit is 400 parts per million, but 30 parts per million corresponds to the lower limit of the "dangerous" category established by the EPA. After 2 hours running, 55 percent of the CO was removed. Given the brief contact time, a per-pass filter efficiency of 14.6 percent may be calculated. An LTC filter removed 78 percent CO in 2 hours.

Ozone

An LTC-only filter in the appliance was run in the sealed room containing 164 parts per billion ozone (STEL limit is 300 parts per billion). After 38 minutes, 99+ percent was removed. Other tests indicate that the very reactive ozone molecules are decomposed to oxygen by chemisorption and subsequent interaction on the alumina surface, as well as the LTC active sites.

Nitric Oxide

An LTC filter was exposed to 20 parts per million NO at 300 cfm (STEL is 35 parts per million). After 80 minutes, the LTC had removed 20 percent, whereas the LTC/carbon filter was able to remove 40 percent of the initial concentration.

Nitrogen Dioxide

The LTC filter was exposed to 4 parts per million NO_2 (STEL is 5 parts per million). Removal was 40 percent after 100 minutes versus 100 percent removal for the LTC/carbon filter. The NO_2 molecules seem to be more tightly adsorbed to active carbon surfaces than to the LTC/alumina surfaces. As shown in Figure 2, increasing temperatures increase the rate of desorption (tube tests).

Sulfur Dioxide

An LTC filter in our appliance was run in the sealed room containing 5 parts per million SO_2 (STEL is 5 parts per million). Removal of 100 percent was achieved after 90 minutes. Other tube tests⁴ have shown that SO_2 is chemisorbed by LTC active Cu(II) sites until saturation.

Hydrogen Sulfide

The LTC filter was subjected to 4 parts per million H_2S (STEL is 15 parts per million). After 60 minutes, about 100 percent of the H_2S was removed. Earlier tube tests (unpublished data, Western Kentucky University, September 1983) indicate an irreversible reaction of H_2S with LTC which results in a gradual poisoning of the active sites. Apparently, copper sulfide is the reaction product.⁴

Ammonia

An LTC filter in the air filtration appliance was run in an atmosphere containing 140 parts per million of ammonia. An STEL recommended limit of 35 parts per million is published. After 60 minutes, 58 percent was removed; 76 percent at the end of the 2 hour test. Subsequent, continuing test runs show that the catalyst is gradually saturated, with NH_3 removal dropping to 6 percent after 6 hours.

Benzene

The LTC filter was exposed to 17 parts per million of benzene vapor in the test room (STEL limit is 25 parts per million). Only 8 percent was removed after 2 hours, whereas the LTC/carbon filter was able to remove greater than 90 percent of the benzene concentration, even after each of five successive test runs. The benzene molecule is non-polar and readily adsorbed by the porous activated carbon. The LTC is relatively unreactive to the benzene structure.

Components of Tobacco Smoke

Chemical components of both mainstream and sidestream tobacco smoke are present in air as particulate or aerosol and a gaseous phase. The major portion of particulate is tar, nicotine, and water; the majority of the gas phase is carbon dioxide, carbon monoxide and methane. Particulate can be removed mechanically from mainstream smoke by a paper filter (cigarettes).

Table II lists some of the higher concentration constituents of tobacco smoke along with their biological effects.

TABLE II
Some cigarette smoke gaseous constituents
Mainstream smoke: unfiltered cigarette^a

<u>Gas Phase Components</u>	<u>Biological Activity</u>	<u>Wt/Cigarette</u>
Carbon Dioxide		10-60 mg
Carbon Monoxide	Toxic	10-20 mg
Methane		1.3 mg
Acetaldehyde	Toxic	770 mg
Acetone		100-600 mg
Nitrogen Oxides	Toxic	60-600 mg
Isoprene		582 mg
Hydrogen Cyanide	Toxic	430 mg
2 - Butanone		80-250 mg
Acetonitrile		120 mg
Toluene		180 mg
Ammonia	Toxic	80 mg
Benzene	Co-Carcinogen	67 mg
Acetylene		27 mg
Dimethylnitrosamine	Carcinogen	10-65 mg
Nitrosopyrrolidine	Carcinogen	10-35 mg

a - U.S. Dept. of Health, Education & Welfare, "The Health Consequences of Smoking", 1981.

The most acute biological effect of tobacco smoke is suffered first from nicotine, and secondly from carbon monoxide. The latter markedly decreases the oxygen-carrying capacity of the blood and may impair the nervous system functions. Its effects range from inducing headaches and dizziness to implication in heart attacks and strokes.⁹

Room Test for CO From Cigarette Smoke

The test results for CO removal from sidestream cigarette smoke using the Instapure® Air Filter (AF-1) are shown in Figure 5. Two cigarettes were smoked every half-hour in a 1152 cubic foot sealed room to generate the upper curve ending at 48 parts per million CO in 8 hours. The same procedure was followed while running the AF-1 appliance, which gave the center curve (32 parts per million CO at 8 hours). The lower curve is for a repeat of the second test with cigarette smoking terminated after 6 hours. The air filter removes 34 percent of the cumulative CO concentration.

Mainstream Smoking Test

A small filter containing 6 grams of LTC was attached to unfiltered cigarettes to test for removals of mainstream tobacco smoke components. The

tests were conducted by an independent laboratory and are summarized in Figure 6. Oxidation of CO is dramatic--from 17,000 to 430 parts per million with the LTC filter. Referring to Table II, several other hazardous compounds are significantly reduced by use of LTC. Acetaldehyde and ammonia are diminished from 1,600 to 18 and 160 parts per million or less respectively. Likewise, methyl chloride and methyl ethyl ketone are removed in majority. Acetone and methyl alcohol are mechanically removed; several constituents are below the detection level and therefore show no change.

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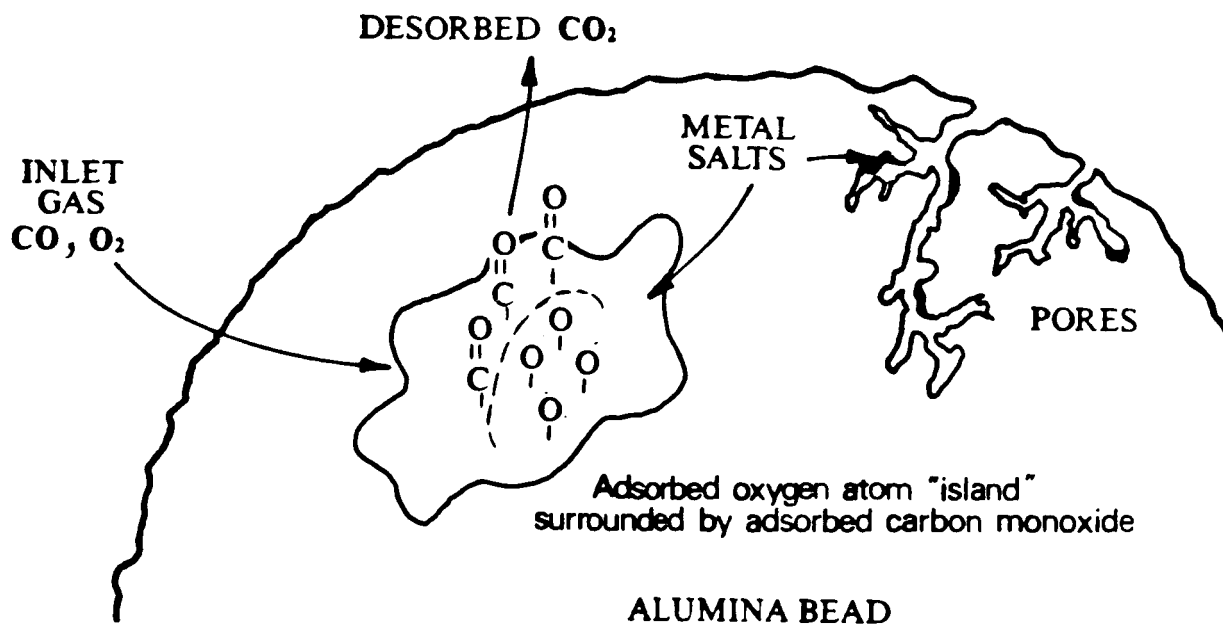


Figure 1. Diagram of catalytic CO oxidation mechanism.

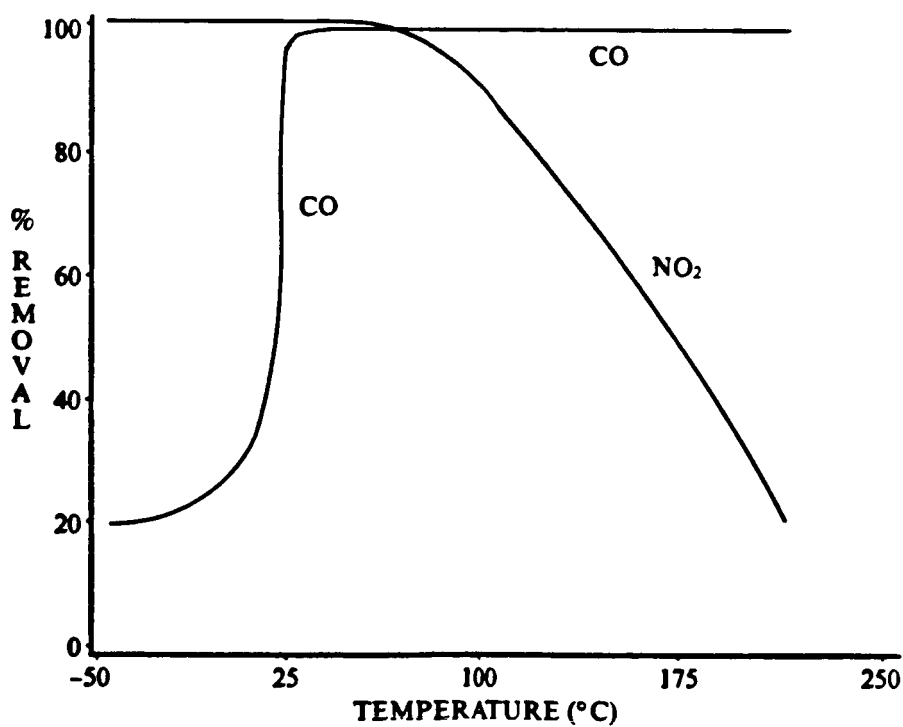


Figure 2. LTC removal of CO and NO₂ as a function of temperature.

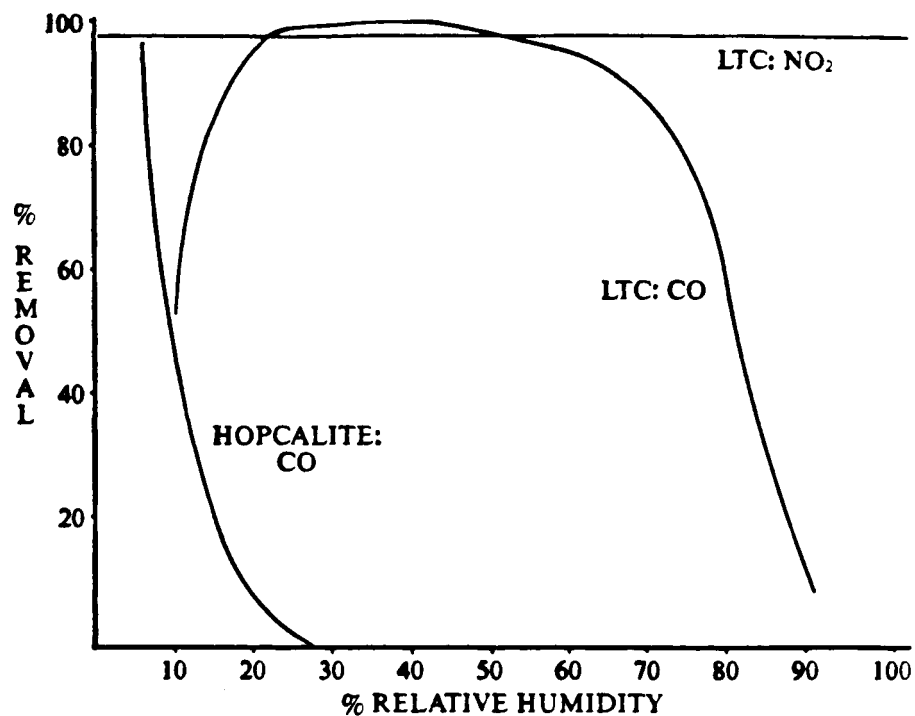


Figure 3. Catalyst removals as a function of relative humidity.

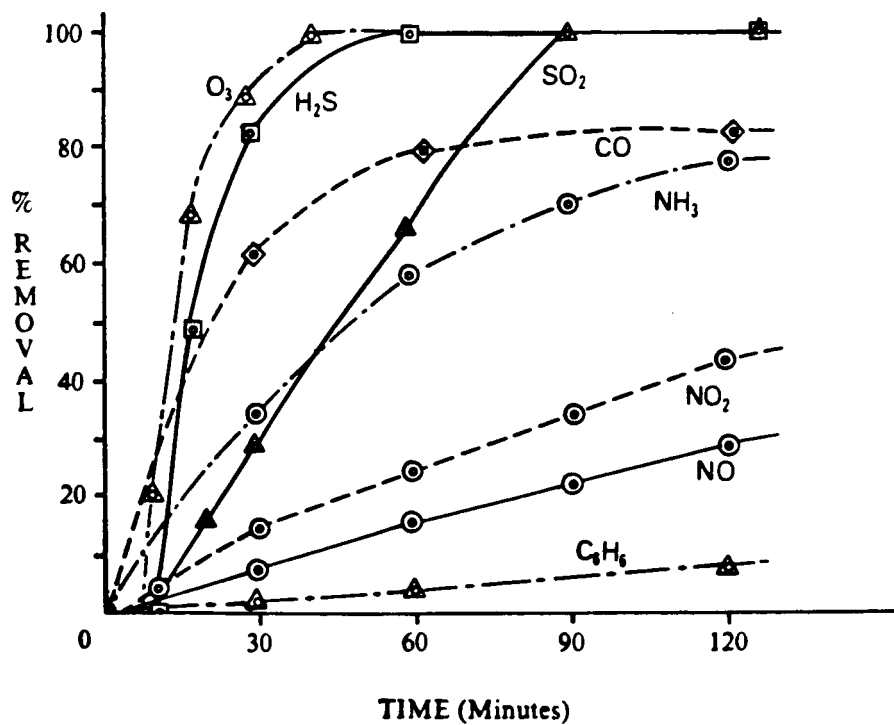


Figure 4. Room test of LTC filter for various contaminants.

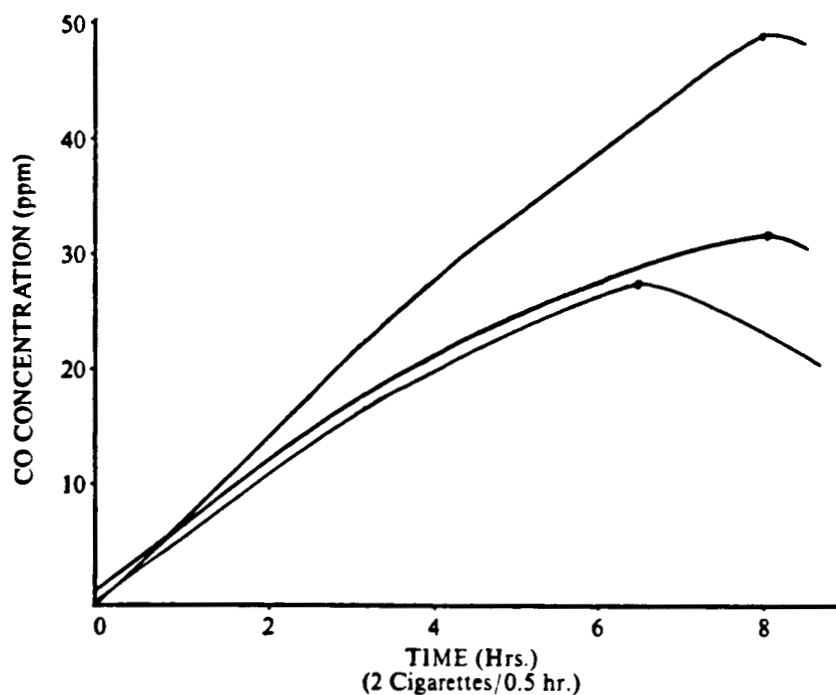


Figure 5. Room tests of product filter for CO (smoke) removal rate.

<u>POLLUTANT</u>	<u>CIGARETTE (ppm)</u>	<u>LTC/CIGARETTE (ppm)</u>
Carbon monoxide	17,000	430
Hydrocarbons	2,700	600
Ammonia	1,600	160
Acetaldehyde	1,600	< 18
Methyl chloride	550	84
Acetone	480	< 7
Methyl alcohol	350	< 60
Methyl ethyl ketone	100	< 6
Hydrogen sulfide	41	< 1

Figure 6. LTC removal of contaminants in cigarette smoke.